

10/624,913

2-12-4

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 762 473 A3

(12)

EUROPEAN PATENT APPLICATION

(88) Date of publication A3:
07.05.1997 Bulletin 1997/19

(51) Int. Cl.⁶: H01J 49/04, G01N 30/72

(43) Date of publication A2:
12.03.1997 Bulletin 1997/11

(21) Application number: 96114339.3

(22) Date of filing: 06.09.1996

(84) Designated Contracting States:
DE GB

(30) Priority: 07.09.1995 JP 229891/95

(71) Applicant: HITACHI, LTD.
Chiyoda-ku, Tokyo 101 (JP)

(72) Inventors:
• Hirabayashi, Atsumu
Hachioji-shi (JP)
• Hirabayashi, Yukiko
Kokubunji-shi (JP)

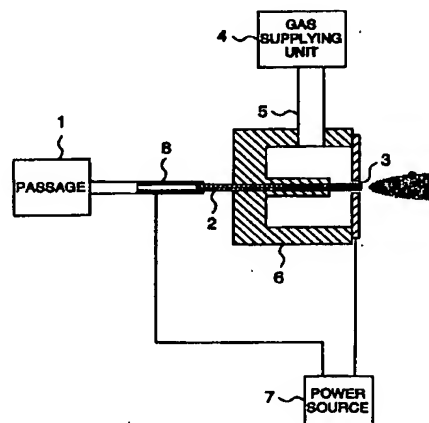
- Sakurai, Minoru
Tokorozawa-shi (JP)
- Takada, Yasuaki
Kokubunji-shi (JP)
- Nabeshima, Takayuki
Kokubunji-shi (JP)
- Koizumi, Hideaki
Setagaya-ku, Tokyo (JP)

(74) Representative: Strehl Schübel-Hopf Groening &
Partner
Maximilianstrasse 54
80538 München (DE)

(54) Mass spectrometer and mass spectrometry for analysing compounds contained in a solution

(57) A mass spectrometer employing an ion source (6) includes a capillary (2) for spraying therethrough liquid into the atmosphere, and an orifice (3) through which a portion in the vicinity of a tip of the capillary is inserted, the orifice being designed in such a way that gases are caused to flow up to the tip of the capillary along a peripheral wall face of the capillary. The flow rate of gas in the vicinity of the tip of the capillary is about the sonic velocity, and a voltage is applied across the liquid flowing through the capillary and the orifice or an electrode (9, 12) arranged in the vicinity of the tip of the capillary.

FIG. 1



EP 0 762 473 A3



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 11 4339

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|--|---|---|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
| X | INTERNATIONAL JOURNAL OF MASS SPECTROMETRY AND ION PROCESSES, vol. 136, no. 2/03, 22 September 1994, pages 167-180, XP000502722 WILM M S ET AL: "ELECTROSPRAY AND TAYLOR-CONE THEORY, DOLE'S BEAM OF MACROMOLECULES AT LAST?" | 1,6,7 | H01J49/04 G01N30/72 |
| A | * page 169, left-hand column, last paragraph - right-hand column, paragraph 2; figure 2 * | 8-21, 26-31 | |
| A | --- US 5 223 226 A (WITTMER DOUGLAS P ET AL) 29 June 1993 * column 5, line 33 - line 48 * | 1,6,7 | |
| D,A | --- ANALYTICAL CHEMISTRY, vol. 59, no. 22, 1987, pages 2642-2646, XP002020246 A. P. BRUINS ET AL.: "Ion spray interface for combined liquid chromatography / atmospheric pressure ionization mass spectrometry" * page 2643, left-hand column; figure 1 * | 1 | |
| D,A | --- US 5 130 538 A (FENN JOHN B ET AL) 14 July 1992 * column 9, line 19 - column 10, line 7; figure 1 * | 1,21-25 | |
| D,A | --- ANALYTICAL CHEMISTRY, vol. 66, no. 24, 15 December 1994, pages 4557-4559, XP000485677 ATSUMU HIRABAYASHI ET AL: "SONIC SPRAY IONIZATION METHOD FOR ATMOSPHERIC PRESSURE IONIZATION MASS SEPECTROMETRY" * page 4557 - page 44558, left-hand column; figures 1,2 * | 7,9,20, 21, 26-28,30 | |
| | --- -/-- | | |
| The present search report has been drawn up for all claims | | | |
| Place of search THE HAGUE | | Date of completion of the search 9 December 1996 | Examiner HULNE S.L. |
| <p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document</p> | | | |

EPO FORM 150 (3.8.1) (P0401)



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 96 11 4339

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|---|---|--|--|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
| D,A | US 4 300 044 A (IRIBARNE JULIO V ET AL) 10 November 1981 * abstract * * column 1, last paragraph - column 2, paragraph 1; figures 1,2 * | 1,6-9, 19-25 | |
| D,A | US 4 861 988 A (HENION JOHN D ET AL) 29 August 1989 * abstract * * column 4, last paragraph; figures 1,2 * | 1,6,7, 21,26-28 | |
| | | | TECHNICAL FIELDS SEARCHED (Int.Cl.6) |
| The present search report has been drawn up for all claims | | | |
| Place of search THE HAGUE | | Date of completion of the search 9 December 1996 | Examiner HULNE S.L. |
| CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background P : non-written disclosure P : intermediate document | | T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document | |

EPO FORM 1503 (01.92) (P0401)



European Patent
Office

CLAIMS INCURRING FEES

The present European patent application comprised at the time of filing more than ten claims.

- ☐ All claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims and for those claims for which claims fees have been paid,
namely claims:
- ☐ No claims fees have been paid within the prescribed time limit. The present European search report has been drawn up for the first ten claims.

LACK OF UNITY OF INVENTION

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions or groups of inventions,
namely:

see sheet -B-

- ☐ All further search fees have been paid within the fixed time limit. The present European search report has been drawn up for all claims.
- ☐ Only part of the further search fees have been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the inventions in respect of which search fees have been paid,
namely claims:
- ☒ None of the further search fees has been paid within the fixed time limit. The present European search report has been drawn up for those parts of the European patent application which relate to the invention first mentioned in the claims,
namely claims: 1, 6-31

**LACK OF UNITY OF INVENTION**

The Search Division considers that the present European patent application does not comply with the requirement of unity of invention and relates to several inventions, or groups of inventions, namely:

1. Claims 1,6-31 : Device for ionizing a sample in a mass spectrometer consisting of a capillary tube with an insulating tip "the part of said capillary through which the solution is caused to flow" being grounded.
2. Claims 2-5 : Device for ionising a sample in a mass spectrometer, comprising a capillary from which the sample is discharged by assistance of a gas flow and a power source to generate a voltage applied to the sample.
3. Claims 32-36 : Device for ionizing a sample in a mass spectrometer, characterized in that multiply charged ions are produced by spraying a solution containing the sample in an uniform electric field.

